CATALYTIC HYDROGENATION OF CO_2 OVER Cu/ZnO/SBA-15 CATALYSTS FOR PRODUCTION OF METHANOL

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by

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LIST OF ABBREVIATIONS

BET	Bruanuer-Emmet-Teller
BJH	Barrett,Joyner and Halenda
EDX	Energy dispersed X-ray
GC	Gas chromatography
GHGs	Greenhouse gases
GHSV	Gas hourly space velocity
GWP	Global warming potential
P	Pressure
P123	Triblock copolymer poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)
RWGS	Reverse water gas shift
SBA-15	Santa Barbara Amorphous
SEM	Scanning electron microscopy
t	Time
TEM	Transmission Electron microscopy
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis

LIST OF SYMBOLS

%	Percentage
µm	Micrometer
Au	Aurum
C	Carbon
Ce	Cerium
CH_3OH	Methanol
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
CuO	Copper oxide
Ea	Activation Energy
Fe	Iron
Ga	Gallium
Ga_2O_3	Gallium oxide
h	Hour
H	Hydrogen atom
H_2	Hydrogen gas
k	Rate constant
K	Degree Kelvin
kg	Kilogram
kJ	Kilo joule

m	Magnesium
Mn	Mangan
MPa	Mega pascal
N_2	Nitrogen gas
N_2O	Nitrous oxide
Na_2CO_3	Sodium carbonate
nm	Nanometer
Pd	Palladium
R	Ideal gas law constant
wt.%	Weight percentage
Zn	Zinc
ZnO	Zinc oxide
ZrO_2	Zirconium Oxide

PENGHIDROGENAN CO_2 BERMANGKIN MENGGUNAKAN MANGKIN Cu/ZnO/SBA-15 UNTUK PENGHASILAN METHANOL

ABSTRAK

Isu-isu pemanasan global telah menjadi kebimbangan utama di seluruh dunia. Punca utama pemanasan global adalah disebabkan oleh jumlah gas rumah hijau yang semakin meningkat di atmosfera terutamanya gas karbon dioksida (CO_2). Penghasilan metanol dari CO_2 dianggap sebagai alternatif kepada kaedah pemencilan CO_2 secara geologi dan lautan yang mahal. Pemangkin Cu/ZnO dilaporkan menjadi aktif untuk pengeluaran metanol dari penghidrogenan CO_2. Untuk kajian ini, objektif utama adalah untuk menghasilkan mangkin Cu/ZnO/SBA-15 beraktiviti tinggi untuk penghidrogenan CO_2 bagi penghasilan metanol. SBA-15 telah disintesis menggunakan kaedah konvensional tanpa melalui langkah hidroterma dan logam Cu/ZnO telah dimuatkan pada sokongan menggunakan kaedah pemendapan bersama. Pencirian telah dijalankan ke atas SBA-15 dan pemangkin disintesis Cu / ZnO / SBA-15. SBA-15 yang disediakan mempunyai morfologi seperti serat dengan luas permukaan BET, luas liang micro, luas liang meso dan isipadu liang 716,98 m^2/g, 188,32 m^2/g, 528 m^2/g dan 0.70 cm^3/g. Cu/ZnO/SBA-15 dengan pada nisbah Cu: ZnO: SBA-15 3: 4: 6 (23.1% berat Cu) telah dipilih sebagai pemangkin terbaik untuk kajian ini dan digunakan untuk kajian proses. Keadaan reaksi terbaik adalah pada jumlah halaju gas setiap jam (GHSV) 3600 h-1, suhu 543 K dan tekanan 5.0 MPa dengan penukaran CO_2 pada 22% dengan hasil metanol 17.0%. Tenaga pengaktifan bagi pengeluaran metanol dari penghidrogenan CO_2 telah ditentukan daripada Arrhenius plot dan tenaga pengaktifan yang dianggarkan adalah 43 kJ / mol.

CATALYTIC HYDROGENATION OF CO_2 OVER Cu/ZnO/SBA-15 CATALYSTS FOR PRODUCTION OF METHANOL

ABSTRACT

Global warming issues had been widely become main concern worldwide. The main cause of the global warming is due to increasing amount of the greenhouse gases in the atmosphere especially carbon dioxide (CO_2) gas. The production of methanol from CO_2 considered as the alternative to the costly geological and oceanic CO_2 sequestration. Cu/ZnO based catalyst had been reported to be active for the production of the methanol from CO_2 hydrogenation. For this study, the main objective was to synthesized high activity of Cu/ZnO/SBA-15 for hydrogenation of CO_2 to produce methanol. SBA-15 support was synthesized using conventional method without the hydrothermal aging and the Cu/ZnO metal was loaded on the support using deposition co-precipitation method. The characterizations been carried out on the synthesized SBA-15 and catalyst Cu/ZnO/SBA-15. The prepared SBA-15 having fibre like morphology with BET surface area, micropore area, mesopore area and pore volume of 716.98 m^2/g, 188.32 m^2/g, 528 m^2/g and 0.70 cm^3/g, respectively. The Cu/ZnO/SBA-15 with Cu:ZnO:SBA-15 ratio 3:4:6 (23.1 wt% Cu) was selected as the best catalyst for this studies and used for the process studies. The best reaction condition was at total gas hourly space velocity (GHSV) of 3600 h^{-1}, temperature 543 K and pressure 5.0 MPa with conversion of CO_2 at 22% with methanol yield of 17.0%. The activation energy for the production of methanol from CO_2 hydrogenation was determined from Arrhenius plot and the estimated activation energy was 43 kJ/mol.

CHAPTER 1

INTRODUCTION

1.1 World climate

1.1.1 Global warming

One of the phenomena that become a great concern worldwide nowadays is global warming. Basically, global warming has been occurring over the past 15000 years on earth. It can be described as a struggle between human progress and nature. Researchers declared that the earth average temperature had been increased 0.4-0.8 ^{0}C and it is predicted that this temperature will increase up to 1.4-5.8 ^{0}C over next hundred years (IPCC, 2007).

The impacts of global warming include accelerated rising of the sea level that leads to flooding, ice melting in the arctic, severe droughts on certain area, longer wildfire that cause more damage to the environment, and health issues (EPA, 2013). The build-up effect from the global warming could alter earth ecological systems that lead to drastic consequences for the world biodiversity including the human race.

Global warming is also referred as the greenhouse effect. This process occurs when the greenhouse gases (CO_2, NO_2, CH_4, NO_3, and halogenated gas) are released into the atmosphere from worldwide activities. These gases are capable of absorbing the infrared radiation. The visible shortwave light from the sun to the earth, passing through the greenhouse gases and the infrared radiation reflects off from the earth's surface towards space and some of it being trapped by the greenhouse gases and

reflected back downwards. The concentration of these gases in the atmosphere keep increasing, trapping heat in the atmosphere, and hence lead to the increasing of average earth temperature.

1.1.2 Greenhouse gases

According to the US Environmental Protection Agency **(**EPA, 2014), the largest constituent of the greenhouse gases is CO_2 which is around 82% as shown in **Figure 1.1**. Other greenhouse gases are methane 9%, nitrous oxide 6% and fluorine-containing halogenated substances (HFCs, PFCs, and SF_6) 3%.

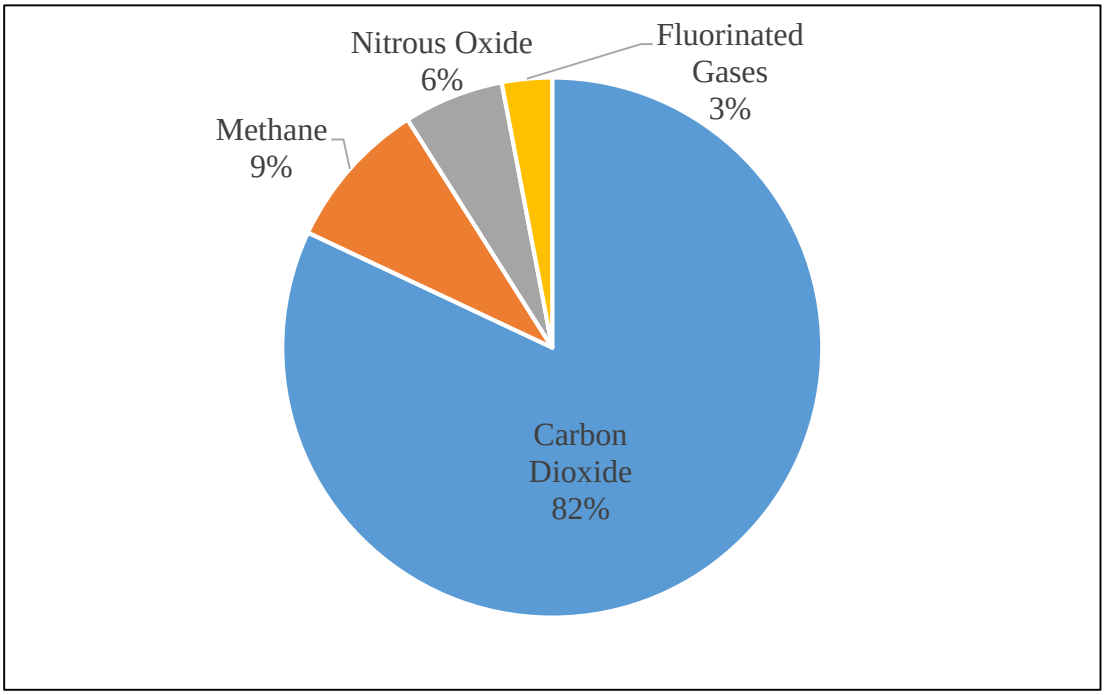

Figure 1.1: Greenhouses gases by emission: Source (EPA 2014)

There are three major properties of greenhouse gases that are considered when evaluating their relative impacts towards global warming and they are the concentration of gases in the atmosphere that reflect on the amount of heat retain in

the atmosphere, the duration to stay in atmosphere that determine their availability to absorb heat and release to the atmosphere, and also their global warming potential (GWP). Global warming potential reflect on how strongly do the gases impact global temperature and is a measured of the total energy that a gas absorbs over a particular period of time (usually 100 years), compared to CO_2 (Forster et al. 2007). According to these factors, CO_2 is considered to have a big impact since it is abundance in the atmosphere and been able to stay there up to thousands of years. Although methane having GWP 21 times higher than CO_2, the amount of CH_4 is much lower and the ability to stay in the atmosphere is only about 10 years.

Greenhouse gases has been emitted to the atmosphere from various human activities as shown in **Figure 1.2**. Over the last 150 years, the concentrations of the greenhouse gases keep increasing. Fossil fuel combustion (coal and natural gases), for providing electricity and transportation, is the major source of greenhouse gases emitted into the atmosphere. In industry, greenhouse gases are emitted from certain chemical reactions for the production of new products. Other source of greenhouse gases includes commercial, residential and agriculture activities.

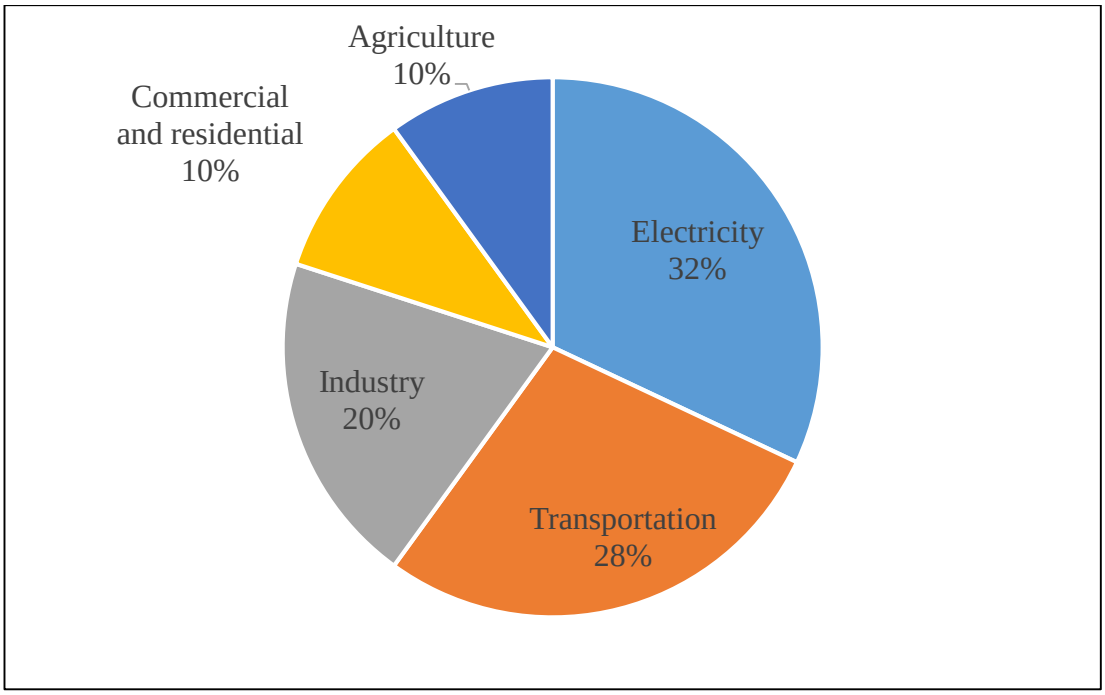

Figure1.2: Total greenhouse gases emission in US. Source (Inventory of U.S Greenhouse Gas Emission and sink, 1990-2012)

1.2 Carbon Dioxide

1.2.1 CO_2 in the atmosphere.

CO_2 is the main gas for the greenhouses gases produced from various human activities that led to climate change and increase in worldwide temperature. In nature, CO_2 exist either as free CO_2 or in combination in carbonate form. The source of CO_2 is mainly from the complete combustion of carbonaceous fuel such as coal, coke, fuel oil, gasoline and cooking gas that were part of human daily activities.

CO_2 is colourless, odourless and tasteless. It does not burn since it is the product of combustion and a very stable compound that make it inert under normal condition towards any reaction. It is also nontoxic compared to carbon monoxide gas. However, if being inhaled in large amount up to 30 %, it could lead to death due suffocation (Aerias, 2005). It is fairly soluble in water and form carbonic acid when dissolved. At very high temperature, CO_2 can decompose into carbon and oxygen.

CO_2 plays an important role in maintaining the biological and ecological system on earth. CO_2 is considered as an important gradient of carbon cycle since it can be produced from human and animal respiration systems and then being used by plants for photosynthesis process. Photosynthesis process that utilized CO_2 for food production for the plant later releasing the oxygen gas for human and animal respiratory systems. However, the abundance of CO_2 due to other sources disturbs the balance of this cycle and lead to environmental pollution.

Before Industrial Revolution in 1760, the concentration of CO_2 was oscillating between 180-280 parts per million (ppm) for over thousands years. The concentration of CO_2 has been steadily increased to above 280 ppm since then as shown in **Figure 1.3** and in December 2014, the atmospheric CO_2 concentration reached 398.78 ppm (NOAA-ESRL, 2015) .The reduction of green plants due to deforestation worldwide decreased the amount of CO_2 absorb by the plant.

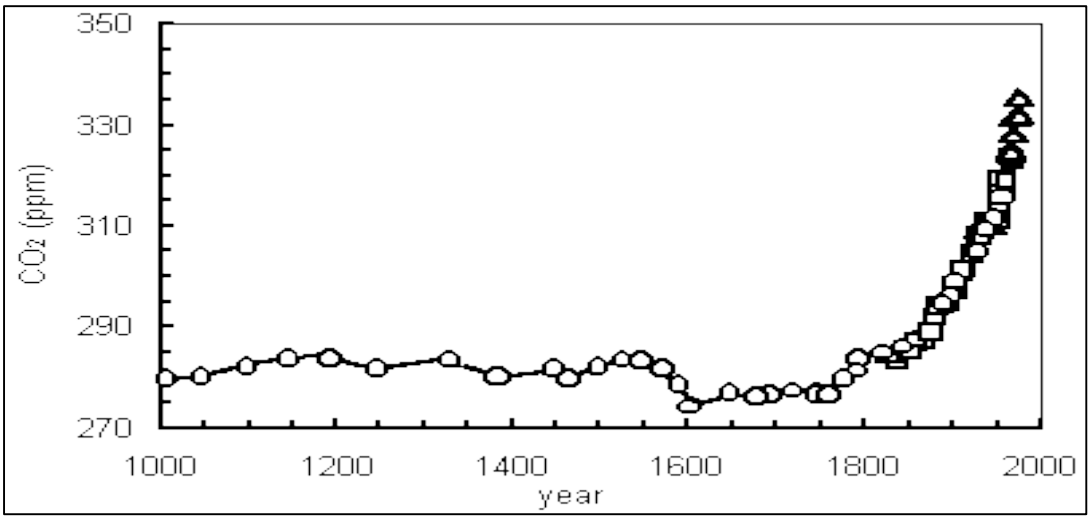

Figure 1.3: CO_2 level trending form year 1000-2000 (CDIAC 2015)

The utilization of CO_2 by conversion into more valuable chemicals becomes a good choice due to the abundant amount of the CO_2 in the atmosphere which ensures a good source for feedstock. CO_2 can become the source for both carbon and oxygen

for various types of chemical group, including alkane, alkene, alcohol, carboxylic acid and other complex chemicals as shown in **Figure 1.4**. CO_2 conversion basically involves the reduction or hydrogenation process where the reactant with hydrogen component such hydrogen gas or methane normally used to react with CO_2.

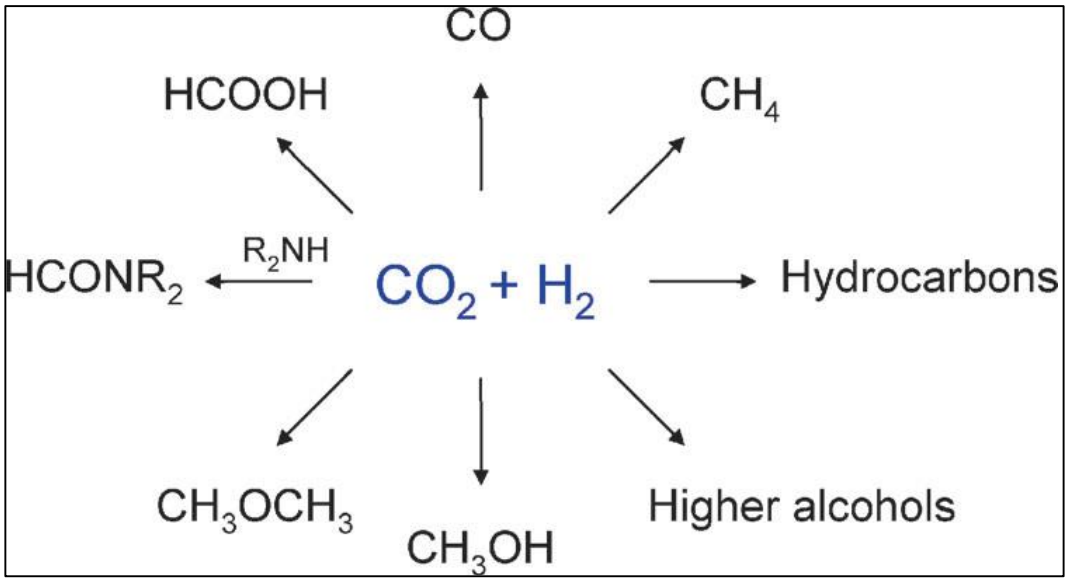

Figure 1.4: Hydrogenation reaction for CO_2 (Wang et al. 2011).

1.3 Catalysis

One of the most important component in organic and inorganic processes nowadays is the catalyst. Catalyst is a substance that is used for the reaction but remain the same as before the reactions. As shown in **Figure 1.5**, catalysts play an important role in providing an alternative route for the reaction that used lower activation energy of a single elementary step which either accelerate the chemical reaction or reduce the reaction temperature and pressure.

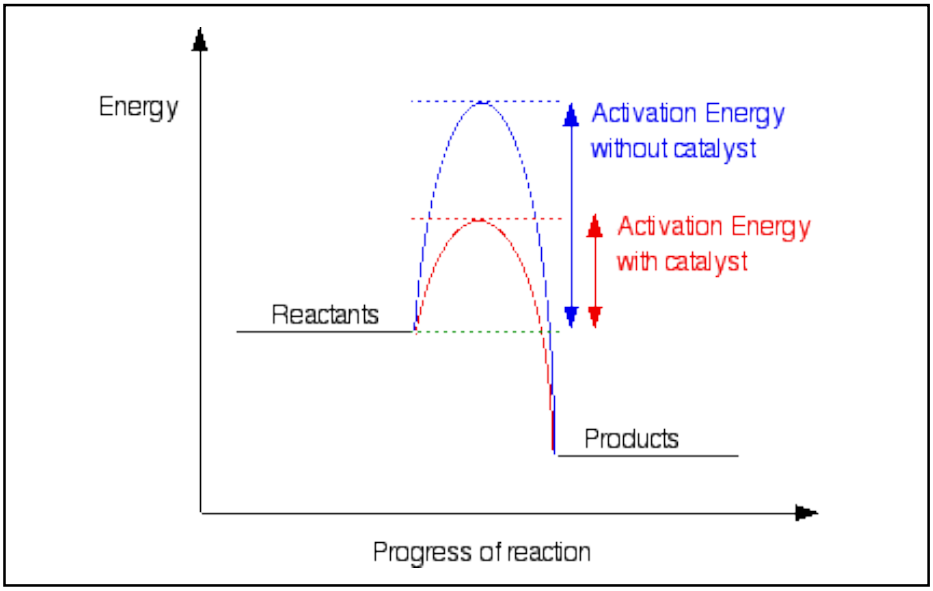

Figure 1.5: Reaction pathway for catalysed and un-catalysed reactions.

There are two types of catalyst which are homogeneous (same phase as the reactant) and heterogeneous (different phase as the reactant). Around 90% of chemical processes use heterogeneous catalysts including chemicals, food, pharmaceutical, automobile, petrochemical industries and more modern fields such as nanotechnology and biotechnology. Heterogeneous catalyst is widely used due to the fact that the catalyst and the reaction production can be separated easily compared to homogeneous catalyst.